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In re Application of

James F. Elman, et al

MULTILAYER OPTICAL
COMPENSATOR, LIQUID
CRYSTAL DISPLAY, AND
PROCESS

Serial No. 10/631,152

Filed 31 July 2003

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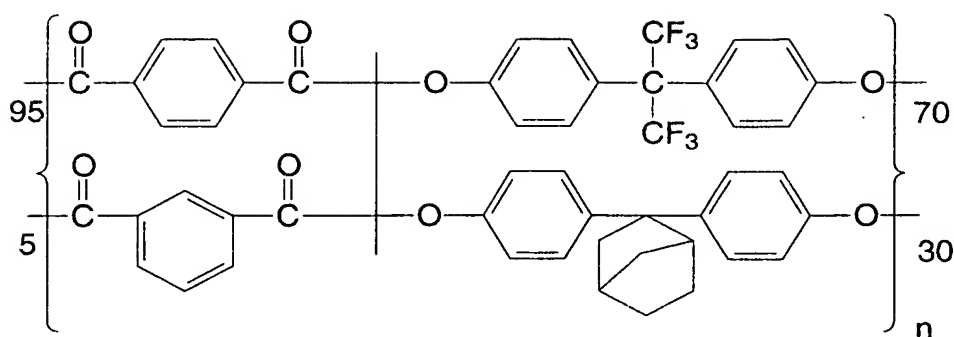
The undersigned, James F. Elman, declares that:

He has received the degree of Ph.D. in Polymer Science from the
University of Connecticut in 1993; a degree of M.S. in Polymer Science from the
University of Connecticut in 1990; and a B.Sc. in Zoology from the University of
Toronto, St. Michaels College (1975);

He has been employed as a research scientist in polymer and imaging
science with Eastman Kodak Company since 1979 and is presently a principal
investigator in the Display Science and Technology Center;

He has obtained X-ray reflection and transmission data for a polymeric
layer useful in the invention having the formula:

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Poly(4,4'-hexafluoroisopropylidene-bisphenol-co- 4,4'-(2-norbornylidene) bisphenol) terephthalate-co-isophthalate.

The polymer was prepared and tested as follows:

To a stirred mixture of 4,4'-hexafluoroisopropylidenediphenol (23.53 g, 0.07 mole), 4,4'-(2-norbornylidene) bisphenol (8.4 g, 0.03 mole) and triethylamine (22.3 g, 0.22 mole) in methyl ethyl ketone (100 mL) at 10° C. was added a solution of terephthaloyl chloride (19.29 g, 0.095 mole) and isophthaloyl chloride (1.02 g, 0.005 mole) in methyl ethyl ketone (60 mL). After the addition, the temperature was allowed to rise to room temperature and the solution was stirred under nitrogen for 4 hours, during which time triethylamine hydrochloride precipitated in a gelatinous form and the solution became viscous. The solution was then diluted with toluene (160 mL) and washed with dilute hydrochloric acid, (200 mL of 2% acid) followed three times by water (200 mL). The solution was then poured into ethanol with vigorous stirring, and a white bead like polymer precipitated, collected and dried at 50° C. under vacuum for 24 hours. The glass transition temperature of this polymer was measured by differential scanning calorimetry to be 270° C.

When the polymer is spun cast onto glass (10% solids in 50% propylacetate 50% toluene), and is then removed from this substrate it shows the following optical retardations. Re, Rth and the polymer III layer thickness are measured with an ellipsometer (model M2000V, J.A. Woollam Co.) at 550nm wavelength.

TABLE IV

Polymer IV Layer thickness (μm)	Re, In Plane Retardation (nm)	Rth, Out of Plane Retardation (nm)
5.9	0.2	-221

He has compared the X-ray spectra for this inventive polymer to the spectra for the polyimide polymers provided in Harris and Ezzell as shown in Figures 1A, 1B, 2A, and 2B, attached, and the results were as follows:

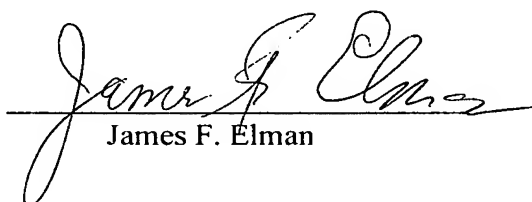
FIG 1A shows X-ray diffraction data (reflection mode) from a polymer film of the present invention and compares it to a polyimide film (FIG 1B, also reflection mode) from FIG 5 of US 5,344,916 (Harris). Both Harris and Ezzell teach similar polyimide films said to have "in-plane orientation" and would be expected to have similar orientation properties. FIG 2A shows X-ray diffraction data (transmission mode) from a polymer film of the present invention and compares it to a polyimide film (FIG 2B, also transmission mode) from FIG 6 of US 5,344,916. The figures from US 5,344,916 show both film and fiber data. The film data are the most relevant for this comparison. These plots have been presented so that their horizontal axes are on the same scale for easy comparison. When one compares X-ray diffraction data from a polymer film of the invention with a polyimide film from US 5,344,916, the difference is obvious. There are no distinct, sharp peaks present in the data from the film of the invention. This distinguishes amorphous materials lacking long-range order from materials that do have ordered structures such as crystals, liquid crystals or rigid rod polymers. These ordered materials do produce sharp X-ray peaks.

In the reflection mode data (FIG 1A) a slight rise in the background is noticeable. This is the so-called "amorphous halo" which is a universal feature in the X-ray diffraction patterns of all amorphous materials. Even liquid water will produce an "amorphous halo". The intensity of the "amorphous halo" observed in an X-ray diffraction pattern will depend upon the thickness of the sample.

In the theoretical sense, there may be some degree of amorphous character to ordered or crystalline polymeric material, but the absence of sharp peaks is accepted as the confirming evidence that a layer meets the definition of

amorphous. The claims of the application are limited to layers that are amorphous and lack long-range order. The polymers of the cited Ezzel reference do not meet this requirement, and those polymers are therefore not amorphous. My conclusion is that the polyimide films said to have "in-plane orientation" in Ezzel (col. 3/ln 29; col. 8/ln 44) and Harris (col. 4/ln 29) are not amorphous as the invention requires.

The undersigned declares further that all statements made herein of the undersigned's own knowledge are true and all statements made on information and belief are believed to be true. These statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 11-15-05 
James F. Elman

Enclosed: Figures 1A, 1B, 2A, and 2B



Industrial Applications of X-Ray Diffraction

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1. INTRODUCTION

X-ray diffraction (XRD) has long been recognized as a valuable tool in various aspects of polymer characterization, for understanding the influence of processing on the properties and performance of polymers. XRD is routinely used in industry to evaluate the degree of crystallinity and preferred orientation, as well as to determine crystal structure and polymorphism. XRD is also used to follow structural changes with temperature, to study crystallization kinetics, and to characterize defects in polymers.

Polymers can be broadly classified as either amorphous or semicrystalline. Amorphous polymers include glassy polymers with sterically hindered chains (e.g., polycarbonate), crosslinked polymers such as thermosets (e.g., epoxy) and elastomers (e.g., rubber). Semicrystalline polymers include thermoplastics (e.g., polyethylene), thermoplastic elastomers (e.g., ethylene vinyl acetate polymers, EVA) that contain physical not chemical crosslinks, and liquid crystalline polymers (LCPs, e.g., aromatic polyamides). The major impact of XRD in the polymer industry has been in the characterization of semicrystalline polymers including LCPs.

When a semicrystalline polymer crystallizes, part of the material remains amorphous. In some instances, especially in poorly crystallized specimens, it is difficult to make an unambiguous distinction between amorphous and crystalline phases (see, e.g., Balta-Calleja and Vonk, 1989). In general, there is a continuum of structures between the extremes of what are generally regarded as amorphous and crystalline phases. Furthermore, there can be clearly distinguishable intermediate phases, mesomorphic structures, especially in oriented polymers. Despite these complexities, a semicrystalline polymer is often described in terms of a simple two-phase model consisting of an amorphous and a crystalline phase. The fraction of the material that is crystalline is usually determined by analyzing an XRD scan. Unlike other methods of crystallinity determinations, the X-ray method does not require either a calibration or a standard.

When a polymer is deformed, either in the polymer melt (such as spinning, extrusion and injection molding) or in solid phase (drawing), both the crystalline and the amorphous domains become oriented. Orientation of the amorphous and crystalline domains is as important as the crystallinity of the polymer in determining the performance of a polymer. Small-angle X-ray scattering (SAXS), is used to determine lamellar spacing in semicrystalline polymers. SAXS is a tool to measure any long-range order over distance scales of 5–100 nm. These measurements include ordering of fibrils in fibers and of aggregates of ionic clusters in ionomers or colloidal suspensions.

In this chapter we provide an overview of the commonly used wide-angle XRD methods in industrial laboratories for analyzing polymers in the form of powders, fibers, films, and molded parts as they are now practiced. In each of the techniques discussed, we briefly mention the principle, illustrate the method with examples, and mention variants of the commonly used techniques. For additional information on many of the topics discussed here, especially when a reference is not cited, we refer the reader to a comprehensive and highly readable textbook by Alexander (1969).

2. INSTRUMENTATION

XRD data are collected on various types of diffractometers and cameras, depending on the nature of the material (fiber, film, powder or molded part) and the purpose for which the data is being collected (quality control, routine analysis, failure analysis, problem solving, or research). Most commonly used instruments are powder diffractometers. Diffractometers can be either one-circle ($\theta/2\theta$ coupled) or two-circle (independently driven θ and 2θ motors) types. These instruments are operated in the parafocus (Bragg–Brentano) geometry when the samples are unoriented or when partial data from oriented samples is adequate. Powder diffractometers can also be run in transmission geometry to obtain more complete data in various directions from oriented samples, though with considerable loss in intensity.

Sealed tubes, rotating anodes, and synchrotron radiation are used as X-ray sources. The wavelength is typically $\sim 1 \text{ \AA}$, and $\text{CuK}\alpha$ (1.542 \AA) is standard for in-laboratory sources. The intensity of the diffracted X-rays is usually measured by step scanning using a proportional or a scintillation detector. One-dimensional straight or curved position-sensitive detectors (PSDs) can provide significant improvement in speed with little loss in resolution. However, to preserve geometric accuracy, data from oriented specimens still need to be collected in $\theta/2\theta$ scanning geometry. Two-dimensional detectors based on image plates, charge-coupled devices (CCDs), or multiwire proportional counters provide the most complete data from oriented polymers with some loss in geometric fidelity.

3. DATA ANALYSIS AND INTERPRETATION

3.1. Crystallinity

XRD scans have been used since the 1940s to determine the weight fraction of the crystalline phase in semicrystalline polymers. In practice, following the method used by Krimm and Tobolsky (1951), a relative measure of crystallinity is determined from the ratio of the area of the crystalline peaks (A_c) to the total scattered intensity over a limited 2θ range in which the total scattering is most intense (typically $5\text{--}35^\circ 2\theta$ with $\text{CuK}\alpha$).

$$CI = A_c 100 / (A_c + A_o) \quad (1)$$

XRD in

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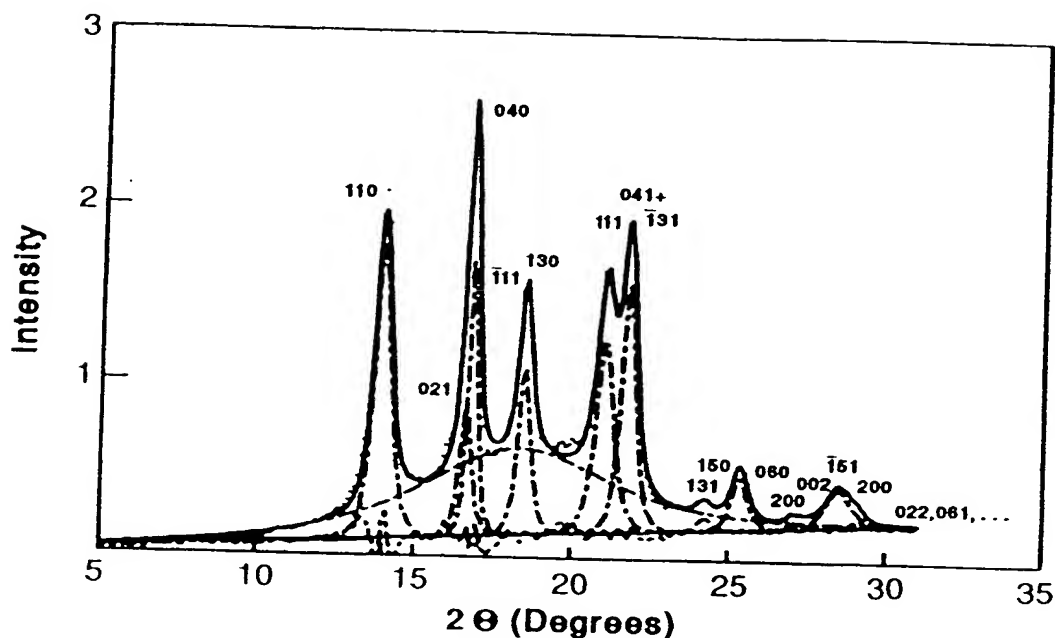
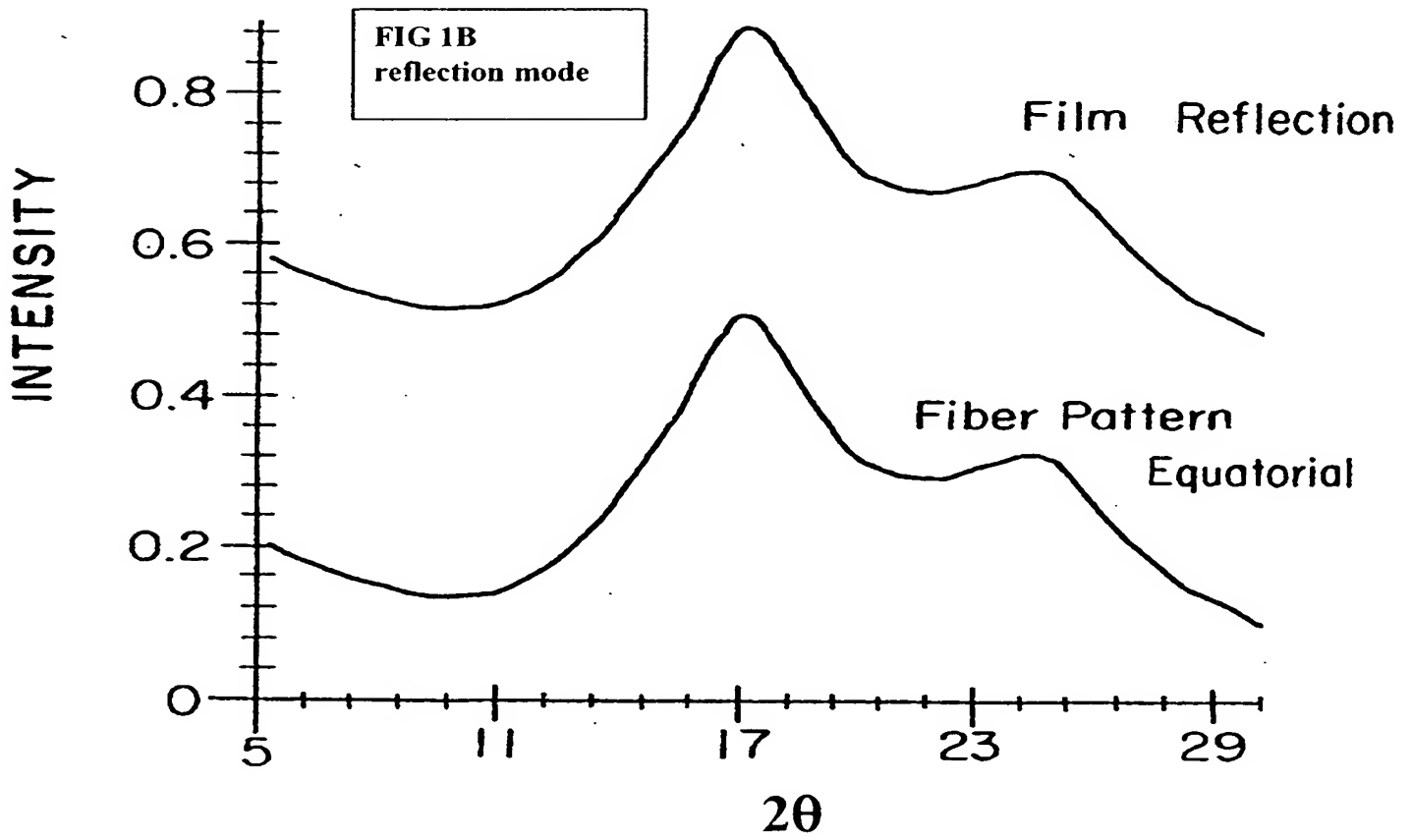
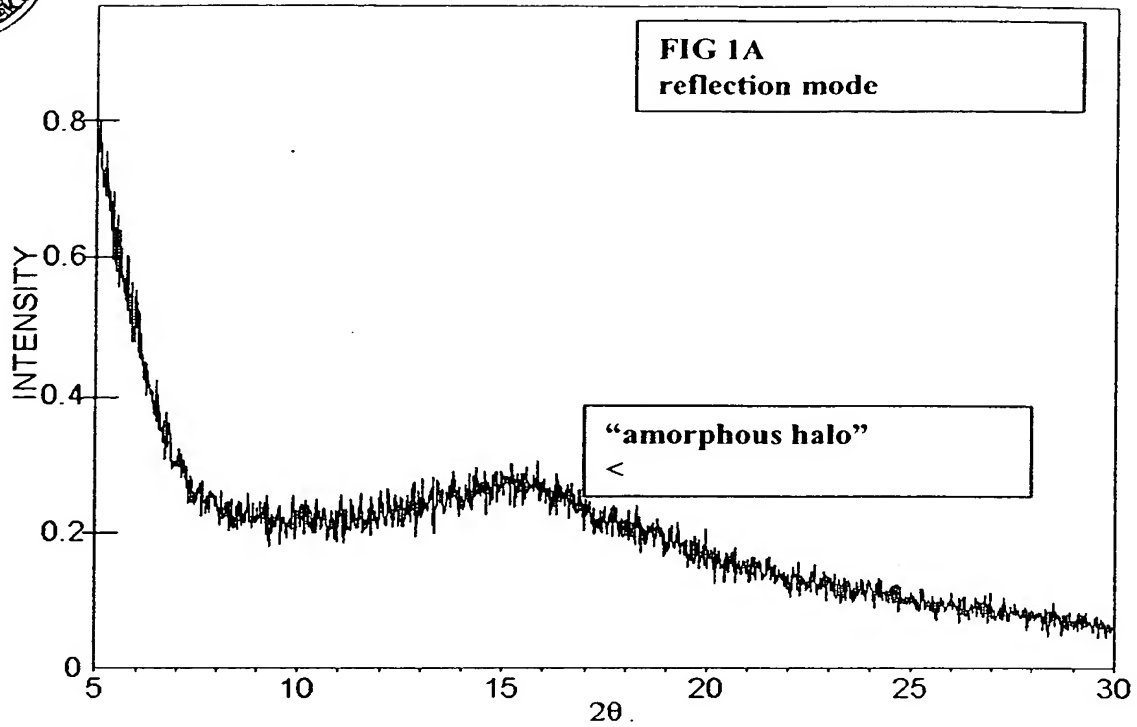
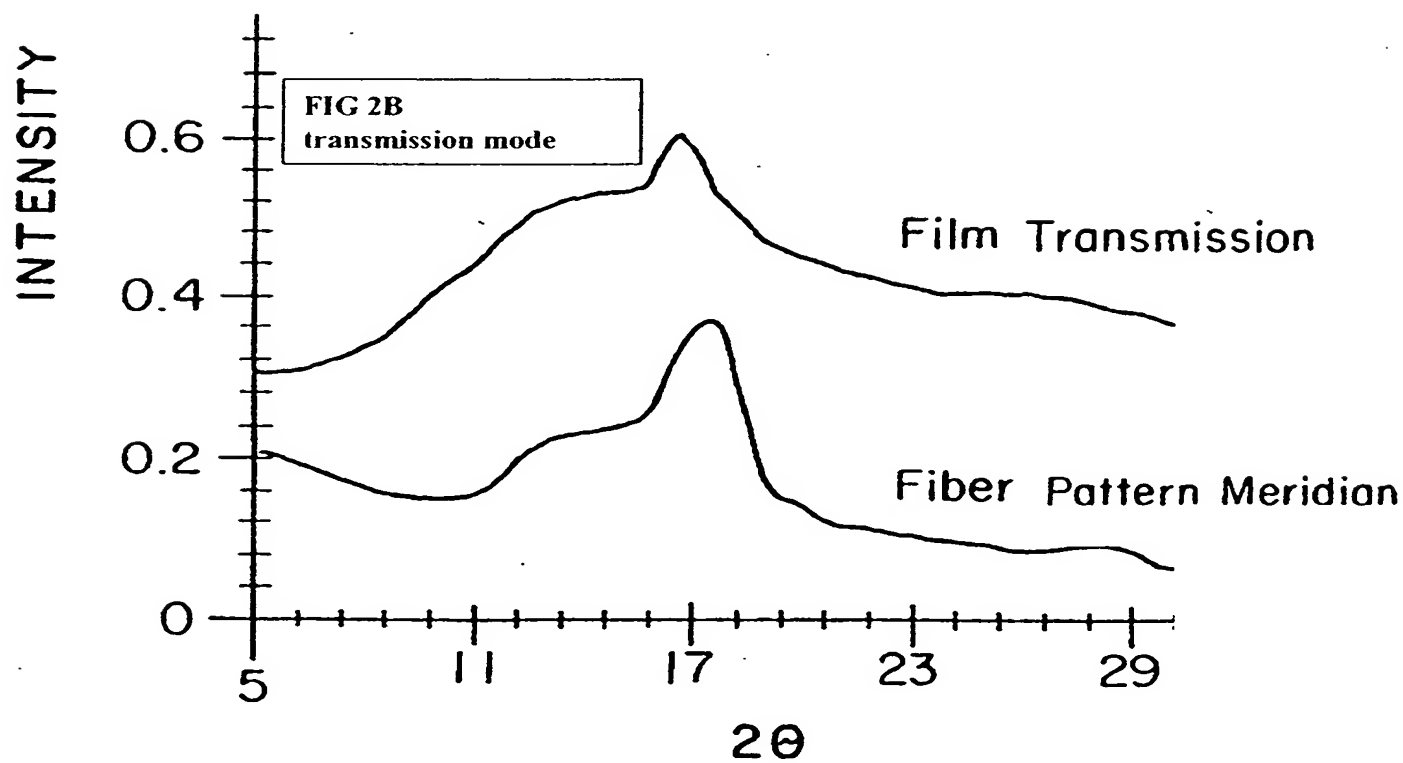
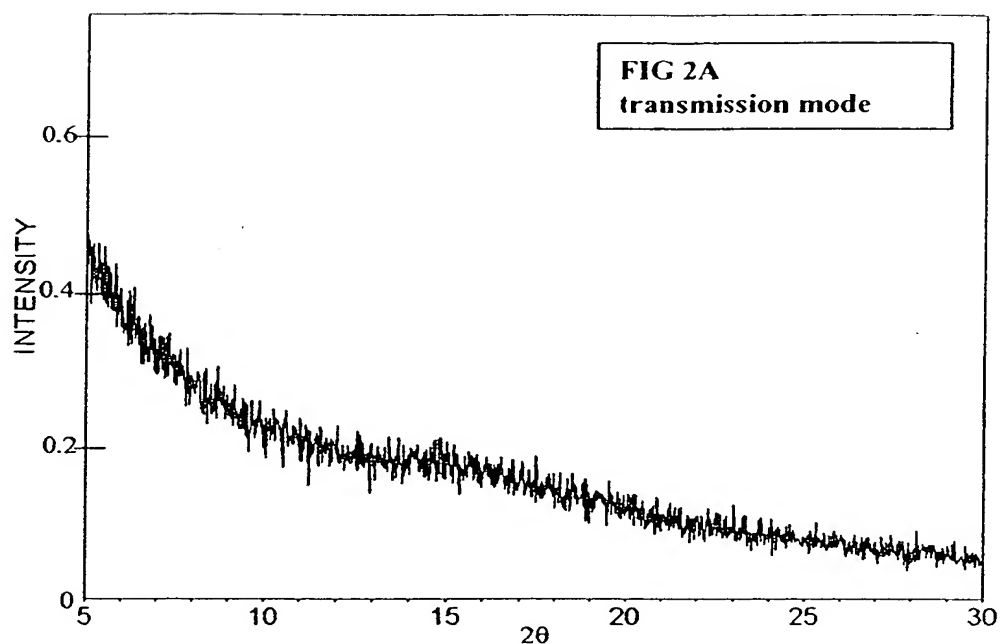


Figure 1 X-ray diffraction scans for polypropylene resolved into amorphous halo and crystalline peaks. The observed data are shown as points, and the solid line through these points is the sum of the resolved components shown in dotted lines. The dashed line over the baseline (shown by solid line) is the difference between the observed intensities and the calculated curve. Reprinted with permission from Murthy (1991).

where $(A_c + A_a)$ is the total scattered intensity, with A_a being the area under the amorphous peak(s). This type of crystallinity is often called a crystalline index (CI) and is expressed as a percentage.

The diffractometer scan is resolved into amorphous and crystalline peaks to determine A_c and A_a (Fig. 1). Three key issues to be addressed in such analysis are defining the baseline, drawing the amorphous halo, and determining the number of crystalline peaks (Murthy, 1997). The baseline in most instances can be assumed to be a straight line in the angular range of interest, but its actual form can be determined by collecting a background scan under conditions similar to that of the sample, and correcting for absorption if necessary (in transmission scans). Drawing a proper amorphous halo has been recognized to be a nontrivial problem for many years (see, for example, Chung and Scott, 1973). The scan from a molten polymer, the first choice, does not provide an ideal amorphous template, although it provides the upper limits of the width and the lower limits of the position of the amorphous halo. Quenching the polymer to an amorphous state is not feasible for many polymers such as nylons, which crystallize rapidly. The most general and versatile method is to extract an amorphous template by stripping the crystalline peaks from a well-crystallized specimen (Murthy and Minor, 1990) as shown in Fig. 2. The third problem, identifying the crystalline peaks, can be addressed by enhancing the resolution of the scan (Murthy and Minor, 1995) as shown in Fig. 3. Reproducible results can be obtained by using the position and the widths of the amorphous peaks, and sometimes even the number and the position of the crystalline peaks, as constraints during least-squares refinement.





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